

Ab initio study of origin and properties of a metal-organic interface state of the PTCDA/Ag(111) system

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We present a detailed study of a monolayer film of 3,4,9,10-perylene-tetracarboxylic acid dianhydride (PTCDA) on Ag(111) (the PTCDA/Ag(111) system). The study is done within density functional theory with the use of the periodic slab model. The slab is chosen to contain a PTCDA monolayer film on a silver thin film of different thicknesses (6, 9, and 12 layers) with the (111) orientation. We show that one of two surface states of the pure Ag(111) films transforms into an unoccupied interface state due to the adsorbate-substrate interaction. The relation of the resulting state to the unoccupied state that has been experimentally observed in the PTCDA/Ag(111) system by scanning tunneling and two photon photoemission spectroscopy is discussed.

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I. INTRODUCTION

Theoretical and experimental investigations of electronic properties of organic molecular structures adsorbed on metal surfaces are of great importance for the solution of both fundamental and practical problems^{1,2}. Among organic molecules, the particular research interest is expressed in 3,4,9,10-perylene-tetracarboxylic acid dianhydride (PTCDA) molecules, since the latters are able to form strictly ordered layers on the surfaces of some metals.^{3,4} When adsorbed on Ag(111), the PTCDA monolayer film causes the appearance of a delocalized two-dimensional band state that in Ref. 5 has been revealed at ~ 0.7 eV above the Fermi level within scanning tunneling spectroscopy (STS) observations. This unoccupied state is described by a parabolic dependence on the two-dimensional electron wave vector \mathbf{k} with the effective mass $m^* = 0.47m_e$, where m_e is the free electron mass. Aiming at understanding the mechanism of electron delocalization in molecular structures, in spite of the similarity of m^* with that of the Shockley surface state (SS) of the pure Ag(111) surface, the authors of the cited work has attributed the origin of such a dispersing state to the substrate-mediated interaction of LUMO+1 orbitals of ordered arrays of the PTCDA molecules. The main experimental evidence of it is that the spatial distribution of the state is concentrated on the molecules and resembles that of the LUMO+1 level of PTCDA. At that the anhydride groups of PTCDA are involved in the wave function of the state.⁵

In Ref. 6, the unoccupied state of the PTCDA/Ag(111) system has been investigated by means of two-photon photoemission spectroscopy (2PPES). The authors of the cited work have presented experimental evidence that the state in question (here with the energy of 0.6 eV above

the Fermi level at $\mathbf{k} = 0$ and with a parabolic dispersion with $m^* = 0.39 \pm 0.03m_e$) comes from the SS of Ag(111). The argumentation in favor of such an origin of the state is that their angle-resolved 2PPES observations reveal the effective electron mass identical to the SS of the pure Ag(111) surface and the location of the state at the metal-organic interface with large bulk penetration comparable to that of the Shockley state. Thus, there are at least two diametrically opposite points of view on the origin of the dispersing unoccupied state in the PTCDA/Ag(111) system. Since such states play a crucial role in the dynamics of excited electrons and charge transfer through the interface^{7,8}, the question of the origin and properties of the unoccupied state in the PTCDA/Ag(111) system is important to be cleared up.

In this paper, within the periodic slab model we study the electronic structure of the PTCDA/Ag(111) system, using *ab initio* density functional theory calculations. The slab is chosen to contain the PTCDA monolayer film on Ag(111) films of different thickness (6, 9, and 12 layers). In the monolayer, the PTCDA molecules are packed in a herringbone structure. On the one hand, we show that the experimentally observed unoccupied state arises from the Shockley surface state, has the bulk penetration similar to that of the latter state, and is localized at the interface. On the other hand, we demonstrate that in the plane of the PTCDA monolayer film the spatial distribution of this interface state is concentrated on the molecules with quite big amplitude on the perylene backbone and anhydride groups and relatively small – at the perylene edges of the PTCDA molecule. Thus, we corroborate the interpretation proposed in Ref. 6 and explain the STS observations of Ref. 5.

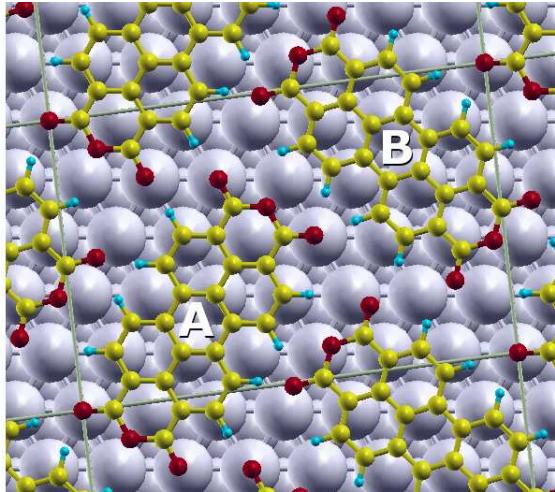


FIG. 1: (Color online) Structure of the PTCDA monolayer on the Ag(111) surface.

II. CALCULATION DETAILS

We use the periodic slab model to study the metal-organic interface. The electronic structure calculations were performed by using the OPENMX code,^{9,10} which are based on the density functional theory (DFT) and a linear combination of localized pseudoatomic orbitals method. We exploit Troullier-Martins type pseudopotentials¹¹ with a partial core correction to replace the deep core potentials by norm-conserving soft potentials. Upper core electrons for the Ag pseudopotential are included in addition to valence electrons in order to take into account the contribution of semicore states to the electronic structure. As a basis set, we take double-valence plus single-polarization orbitals. For hydrogen, carbon and oxygen atoms constituting PTCDA, variationally optimized basis orbitals for biological molecules are used with cut-off radii of 5.0 for C and 4.5 a.u. for O and H atoms.¹² For Ag atoms cut-off radius is 7.5 a.u. The real-space grid techniques are used with the energy cutoff of 190 Ry in numerical integrations and solution of the Poisson equation with the help of the fast Fourier transformation. The total-energy convergence was better than 0.027 meV.

To describe the PTCDA/Ag(111) system, we employ a slab containing a silver film with the (111) orientation and N_l atomic layers ($N_l=6, 9, 12$) together with a PTCDA monolayer film, which is “applied” on one side of the silver film only, and a vacuum region corresponding to 6 silver interlayer spacings. The distance between the silver surface layer and the PTCDA monolayer is taken to be equal to experimental value of 2.86 Å (see Refs. 13 and 14). A close value can be obtained in DFT calculations¹⁵ with exchange-correlation potential in the local density approximation (LDA), while in the generalized gradient approximation the distance becomes very large (~ 3.5 Å in Ref. 13 and 16) and the adsorption energy is under-

estimated. This fact causes the use of the LDA in our DFT calculations.

The PTCDA monolayer on Ag(111) has an ordered periodic structure that consists of two types (denoted as A and B in Fig. 1) of molecules misoriented by an angle of 77° with respect to each other (a herringbone pattern). The A-type molecule is aligned parallel to the row of silver atoms, while the B-type molecule is misaligned by an angle of 17° (see Refs. 17 and 15). The superstructure of the interface is given by a nearly rectangle (a deviation of 1°) unit cell of 18.96×12.61 Å². The resulting periodic supercell of the slab model contains $33 \times N_l$ silver atoms (33 – the number of atoms per layer) and 76 atoms belonging to two PTCDA molecules. The Brillouin zone of the supercell is sampled with a (3 × 3 × 1) mesh of \mathbf{k} points. The z -axis is directed normal to the surface of the films.

III. RESULTS AND DISCUSSION

We start with an band-structure analysis of clean Ag(111) films with the supercell that contains $33 \times N_l$ silver atoms in order to identify surface states (SS) in the absence of the energy gap at the $\bar{\Gamma}$ point of the corresponding small surface Brillouin zone and to make sure that characteristics of these states are the same as in the case of the supercell with $1 \times N_l$ silver atoms, which gives the familiar surface band structure for the Ag(111) surface. Note that in the case of a film there are two surface states with different energies caused by bonding-antibonding splitting due to interaction through the film. We distinguish these two states as SS1 and SS2 with energies $E_{SS1} > E_{SS2}$ at the $\bar{\Gamma}$ point. A comparison has shown that the surface-state energies obtained with the $33 \times N_l$ supercell (see Table I) coincide with those found with the $1 \times N_l$ supercell (not presented) within ~ 10 meV, while the bonding-antibonding splitting (ΔE_{clean}) — within ~ 2 meV. As regards the effective masses, their values practically do not vary with the number of atoms per layer.

The mentioned characteristics of the surface states depend on thickness of the film (see Table I). As was expected, ΔE_{clean} decreases rather rapidly with increasing N_l and should vanish at the $N_l \rightarrow \infty$ limit. The energy E_{SS1} tends to reduce, while E_{SS2} seeks to increase. At the same time the effective mass m_{SS1}^* varies weakly with the thickness as compared to m_{SS2}^* . Note that as N_l increases the average energy E_{clean}^{av} becomes closer to the surface-state energy $E_{SS}^{exp} = -63 \pm 1$ meV experimentally observed¹⁸ for the Ag(111) surface and already for the twelve-layer film E_{clean}^{av} differs from E_{SS}^{exp} within ~ 16 meV.

Now we consider the PTCDA monolayer on the Ag(111) film of different thicknesses. Fig. 2 shows the obtained band structure for two cases: nine- and twelve-layer silver films. Also, the figure reflects our results on analysis of the square modulus of wave functions of found

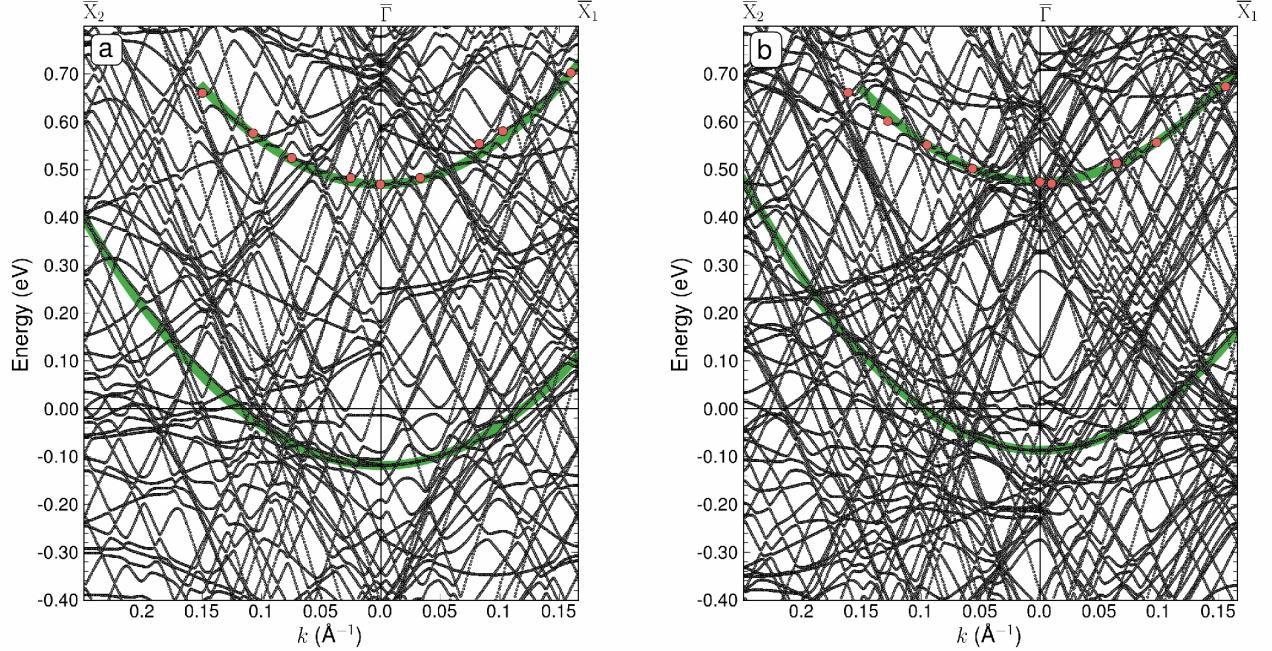


FIG. 2: (Color online) Band structure of the PTCDA monolayer on the nine- (a) and twelve-layer (b) Ag(111) film in the $\bar{X}_2 \rightarrow \bar{\Gamma} \rightarrow \bar{X}_1$ direction of the surface Brillouin zone. The thick gray lines show the parabolic approximation of the dispersion of the interface (upper line) and surface (lower line) states. Points indicate wave vectors \mathbf{k} , at which the spatial distribution of the interface-state wave function is analyzed (see Table II and Fig. 3).

TABLE I: Energies E_{SS1} and E_{SS2} of the surface states at the $\bar{\Gamma}$ point and corresponding effective masses m_{SS1}^* and m_{SS2}^* for clean Ag(111) films with different number of layers (N_l). $\Delta E_{clean} = E_{SS1} - E_{SS2}$ and $E_{clean}^{av} = E_{SS2} + \Delta E_{clean}/2$. In the case of the PTCDA monolayer on the Ag(111) films, E_{IS} and E_{SS} are the $\bar{\Gamma}$ -point energies of the interface and surface state with effective masses m_{IS}^* and m_{SS}^* , respectively. $\Delta E = E_{IS} - E_{SS}$ and $E_{av} = E_{SS} + \Delta E/2$. All the energies are measured electron volts from the Fermi energy.

Ag(111)						
N_l	E_{SS1}	m_{SS1}^*	E_{SS2}	m_{SS2}^*	ΔE_{clean}	E_{clean}^{av}
6	0.141	0.40	-0.460	0.53	0.601	-0.159
9	0.022	0.38	-0.227	0.46	0.250	-0.102
12	-0.023	0.38	-0.135	0.42	0.112	-0.079
PTCDA/Ag(111)						
N_l	E_{IS}	m_{IS}^*	E_{SS}	m_{SS}^*	ΔE	E_{av}
6	0.523	0.43	-0.271	0.76	0.694	0.176
9	0.469	0.42	-0.119	0.46	0.588	0.175
12	0.474	0.46	-0.087	0.42	0.561	0.193

states (see the thick lines). When averaged over spatial coordinates xy at different \mathbf{k} along $\bar{\Gamma} \rightarrow \bar{X}_2$ and $\bar{\Gamma} \rightarrow \bar{X}_1$ directions, the square modulus can be considered as a function of z , which gives important information about charge-density distribution [denote as $\rho(z, \mathbf{k})$] along the direction normal to the surface. We have thus revealed the partly occupied surface state (the lower thick line in Fig. 2) with the wave function localized in the region of the “clean” surface of the Ag(111) film. At the $\bar{\Gamma}$ point,

the energy (denote as E_{SS}) of such a state depends on the film thickness and, as is seen from Table I, tends to E_{clean}^{av} with increasing N_l . This surface state is originated from the state marked as SS2 in the case of the clean Ag(111) films. Note that in spite of the difference $E_{SS} - E_{SS2}$, which is caused by the presence of the PTCDA monolayer and decreases with an increase of N_l (see Table I), the effective masses m_{SS}^* and m_{SS2}^* are the same (except for the six-layer silver film). At that, for the twelve-layer silver film they become very close to the experimental value of $0.40m_e$ for the surface-state effective mass found for the Ag(111) surface from photoemission data in Ref. 18.

On analyzing $\rho(z, \mathbf{k})$, also we can unambiguously say that in the spectrum above the Fermi level there is an interface state (the upper thick line in Fig. 2) whose wave function has a pronounced maximum in the region of the metal-organic interface (see Fig. 3) and a surface-state-like penetration into the silver film. Actually, as is seen from Table II, more than 50% of the IS charge accumulates in the metal film. The rest of the charge are divided among the interface and molecular-monolayer regions as $\sim 2/3$ and $\sim 1/3$, respectively. As to the energy E_{IS} of the interface state (IS) at the $\bar{\Gamma}$ point, we note that E_{IS} , which is about 0.5 eV, is quite stable with respect to the film thickness (see Table I). The dispersion of the interface state is adequately described by a quadratic dependence on the wave vector \mathbf{k} with an effective mass m_{IS}^* , which is close to that for the aforementioned surface state for $N_l > 6$.

To all appearances, the presented analysis corroborates

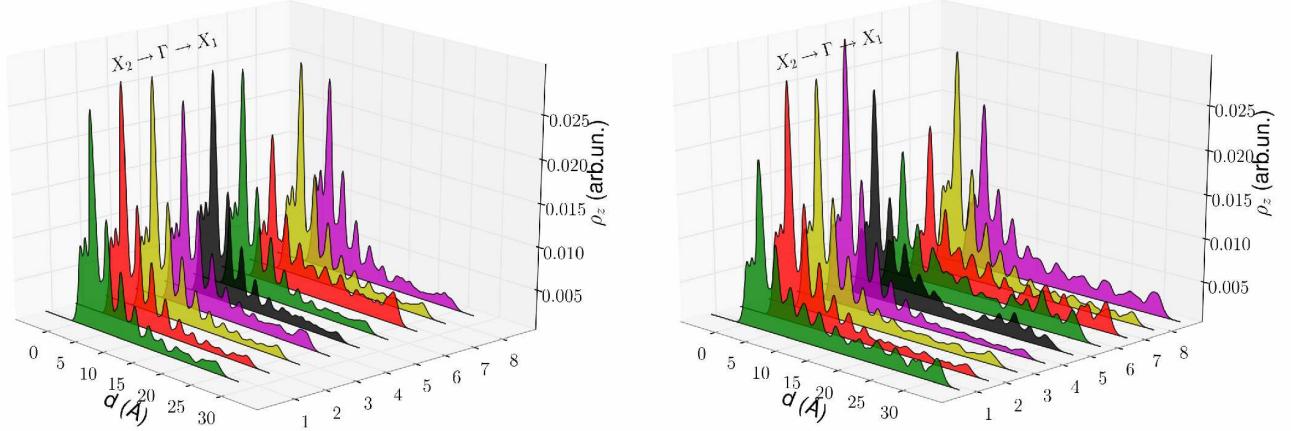


FIG. 3: (Color online) Unity-normalized charge-density distribution $\rho_{IS}(z, \mathbf{k})$ for the interface states as a function of z for different \mathbf{k} in the $\bar{X}_2 \rightarrow \bar{\Gamma} \rightarrow \bar{X}_1$ direction. (a) The PTCDA monolayer on the nine-layer Ag(111) film. (b) The PTCDA monolayer on the twelve-layer Ag(111) film. The distributions for different k -points shown in Fig. 2 are presented in order from left to right in correspondence with k -points listed in Table I in order from top to bottom.

TABLE II: Charges of the interface state in regions of the silver film (Q_b), the interface (Q_i), and the PTCDA monolayer film (Q_m) at different values of \mathbf{k} along the $\bar{X}_2 \rightarrow \bar{\Gamma} \rightarrow \bar{X}_1$ direction of the surface Brillouin zone (see points in Fig. 2). Two cases of nine- and twelve-layer silver films are presented. To calculate the charges, the unity-normalized charge-density distribution $\rho_{IS}(z, \mathbf{k})$ shown in Fig. 3 has been used.

$N_l = 9$				$N_l = 12$			
$k, \text{Å}^{-1}$	Q_b, e	Q_i, e	Q_m, e	$k, \text{Å}^{-1}$	Q_b, e	Q_i, e	Q_m, e
0.150	0.53	0.30	0.17	0.161	0.66	0.22	0.12
0.107	0.50	0.33	0.17	0.128	0.53	0.30	0.17
0.075	0.51	0.32	0.17	0.095	0.55	0.29	0.16
0.025	0.55	0.29	0.16	0.057	0.51	0.33	0.16
0.00	0.49	0.32	0.19	0.00	0.60	0.27	0.13
0.033	0.51	0.32	0.17	0.010	0.72	0.18	0.09
0.083	0.66	0.22	0.12	0.065	0.70	0.20	0.09
0.103	0.52	0.30	0.18	0.098	0.53	0.29	0.17
0.160	0.53	0.27	0.20	0.156	0.65	0.22	0.13

the interpretation of Ref. 6, in which the unoccupied dispersing state of the PTCDA/Ag(111) system is considered as a genuine interface state arising from an upshift of the occupied Shockley surface state of the clean Ag(111) surface. In fact, as our results show, there is no other unoccupied state, which we could associate with the state discussed in Refs. 6 and 5. In our case, the only interface state we have found can be considered as a transformation of the surface state that is marked as SS1 in the case of the clean Ag(111) films. The transformation is caused by the interaction of the Ag(111) film with the PTCDA monolayer.

Now, in order to establish a connection of our results with the STS observations of Ref. 5, we should trace the transformation of molecular orbitals upon moving from a free PTCDA molecule to the PTCDA/Ag(111) system. To this end, we analyze energies, charge-density distri-

butions $\rho(z, \mathbf{k} = 0)$, and spatial distributions of corresponding states in the molecular plane. We recognize electronic states in the PTCDA/Ag(111) system as those originated from molecular levels from the localization of the wave function predominantly on the PTCDA monolayer. Fig. 4 shows our results of such an analysis. As follows from the figure, the LUMO level of the free molecule [with the structure as it appears in the PTCDA monolayer on Ag(111)] goes down under the Fermi level of the PTCDA/Ag(111) system and splits due to the presence of two types of molecules (A and B) in the unit cell (see Fig. 1). At that the spatial distribution, which is slightly modified under the influence of intermolecular interaction and adsorbate-substrate interaction, preserves practically all its key features. Note that the wave function of the state with smaller energy is predominantly localized on the B-type molecule, while the state with bigger energy is characterized by the wave function, which is mainly localized on the A-type molecule. The nearly degenerate LUMO+1 and LUMO+2 orbitals demonstrate the same tendency. As well as in Refs. 15 and 19, the states originated from these orbitals fix their energies in the vicinity of 1eV. An analysis has shown that the dispersion of these states are very small as compared with that of the found interface state. As regards the spatial distribution of the latter, Fig. 5 clearly shows that, as well as in the case of the states arising from the LUMO+1 and LUMO+2 orbitals, the IS charge density is concentrated on the molecules. However, the character of the distribution on the molecule is quite different. Moreover, in contrast to the states arising from the LUMO+1 and LUMO+2 orbitals, the IS charge density is distributed more or less uniformly among the A- and B-type molecules.

The analysis presented above does not allow us to follow the interpretation of the unoccupied dispersing state of the PTCDA/Ag(111) system, which was made in Ref.

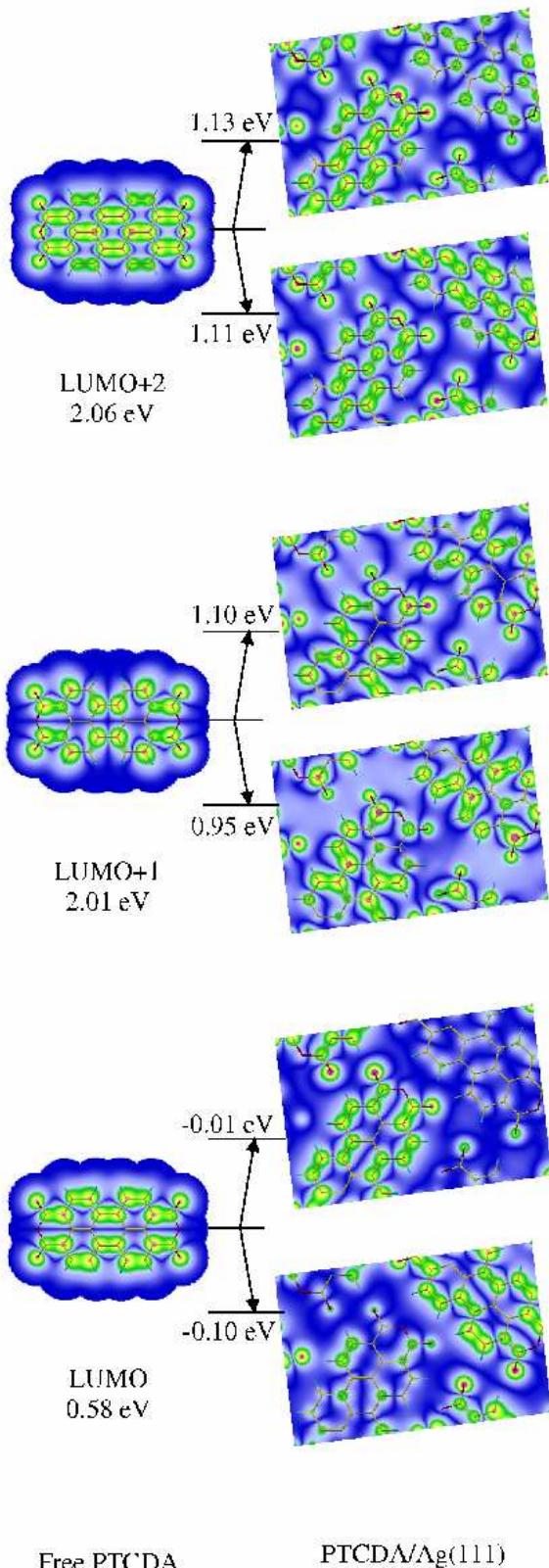


FIG. 4: (Color online) Spatial distribution of three lowest unoccupied orbitals of the free PTCDA molecule (at the left) and corresponding states in the PTCDA/Ag(111) system at the $\bar{\Gamma}$ point in the case of the six-layer silver film (at the right).

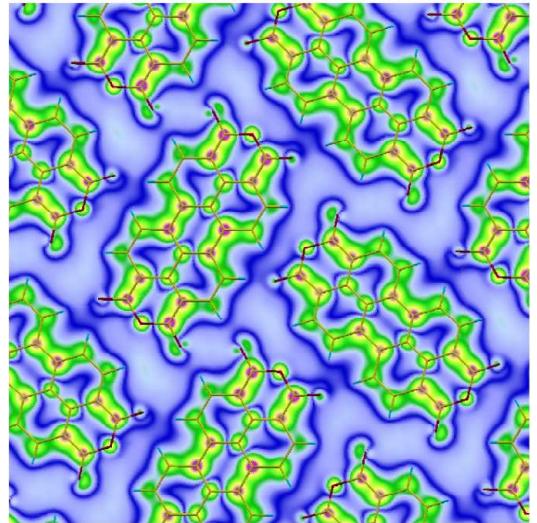


FIG. 5: (Color online) Spatial distribution of the interface state in the PTCDA/Ag(111) system at the $\bar{\Gamma}$ point in the molecular plane for the case of the nine-layer silver film.

5, as the state formed by the molecular orbitals. At that, such main features of the dispersing state, which have been observed in the cited work by the STS, as the dominant localization on the perylene backbone and the involvement of the anhydride groups in formation of the state are clearly seen in Fig. 5. Here we would like to note that in the molecular plane the spatial distribution of the IS does not vary with the silver-film thickness and retains its form as the wave vector \mathbf{k} changes along the symmetric directions of the Brillouin zone.

IV. CONCLUSION

In conclusion, we have investigated electronic structure of the PTCDA/Ag(111) system within density functional theory with the use of the periodic slab model. The slab has been chosen to contain the PTCDA monolayer on the thin Ag(111) film. We have considered the silver films of different thickness (6, 9, and 12 layers) to fix a trend in changes in the electronic structure of the Ag(111) film upon adsorption of the PTCDA monolayer and to check the convergence of our results. We have found that upon the adsorption one of two surface states of the silver film, the wave function of which is localized on the clean side of the film, tends to have the $\bar{\Gamma}$ -point energy as that for the clean Ag(111) surface. Another one transforms into an unoccupied interface state with the wave function that has a pronounced maximum in the region of the metal-organic interface. The interface state has the $\bar{\Gamma}$ -point energy of ~ 0.5 eV, which is weakly varying (within ~ 50 meV) with the silver-film thickness. The dispersion of this state is nearly isotropic and adequately described by a quadratic dependence on the two-dimensional electron wave vector with the effective mass $0.43m_e$, $0.42m_e$ and

$0.46m_e$ for six-, nine-, and twelve-layer Ag(111) film, respectively.

We have related the aforementioned interface state with the unoccupied dispersing state experimentally observed in the PTCDA/Ag(111) system by scanning tunneling⁵ (the effective mass of $0.47m_e$) and two photon photoemission⁶ spectroscopy (the effective mass of $0.39 \pm 0.03m_e$). We have demonstrated that as in the STS observations, in the plane of the PTCDA monolayer film, the spatial distribution of the interface state is concentrated on the molecules with quite large charge density on the perylene backbone and anhydride groups and relatively small – at the perylene edges of the PTCDA molecule. At that, as it has been revealed by the 2PPES, the wave function of this state has a surface-state-like penetration into the silver film. We thus have corroborated the interpretation of the origin of the unoccupied dispersing state of the PTCDA/Ag(111) system, which

has been proposed in Ref. 6.

Finally, we would like to note that in our calculation the unoccupied interface state appears at lower energy than it is experimentally observed (0.7 eV in Ref. 5 and 0.6 eV in Ref. 6). It can be caused by using the LDA to describe electronic states of the metal-organic interface.¹⁹ We believe that as in the case of the free PTCDA molecule (see, e.g., Ref. 20) the *GW* approximation can improve the description of the electronic spectrum of the system under question.

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